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SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF PROVINCIAL WATER QUALITY GUIDELINES FOR ALKYLLEADS

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SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF PROVINCIAL WATER QUALITY GUIDELINES FOR ALKYLLEADS

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Preface

The Ontario Ministry of Environment and Energy develops Provincial Water Quality Objectives or Guidelines for those substances deemed to be of greatest environmental concern in Ontario as determined through a screening process which considered persistence, potential to bioaccumulate, acute and chronic toxicity and potential presence in the aquatic environment. Alternatively, Ministry staff which have a direct responsibility for managing possible effects of these chemicals may request an evaluation. Provincial Water Quality Objectives and Guidelines (PWQO/Gs) are numeric or narrative criteria intended to protect all life stages of aquatic organisms for indefinite exposures and/or to protect recreational uses of water. PWQO/Gs for recreational uses, including swimming, are currently based on microbiological and aesthetic considerations. The potential for harmful effects from exposure to chemical substances during recreational uses will be considered when scientific information becomes available. Ontario Drinking Water Objectives and sport fish consumption guidelines are also considered in protection of human health. PWQO/Gs represent a desirable water quality for the protection of designated uses of surface waters in Ontario. Objectives/Guidelines do not take into account analytical detection or quantification limits, treatability or removal potential, socio-economic factors, natural background concentrations, or potential transport of contaminants among air, water and soil. These factors are considered in policies and procedures which govern the uses of PWQO/Gs, contained in the booklet, Water Management: Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment (MOE 1984), which deals with all aspects of Ontario's water management policy.

The process for deriving these criteria is detailed in Ontario's Water Quality Objective Development Process 1992. The toxicology literature is reviewed for all of the following areas: aquatic toxicity, bioaccumulation, mutagenicity and aesthetic considerations. The final Objective/Guideline is based on the lowest effect concentration reported for any of these factors on aquatic organisms as well as taste and odour considerations of the water. Where there are reliable and adequate data, an Objective is developed using a safety factor. Where there are fewer data, a Guideline is developed using an "uncertainty factor". The size of the uncertainty factor reflects the quality and quantity of data available and the potential of the material to bioaccumulate. Guidelines can be promoted to Objectives when sufficient reliable data become available.

PWQO/Gs are used to designate surface waters of the Province which should not be further degraded. They are also used in receiving water discharge assessments and may be included in Certificates of Approval which are issued to regulate effluent discharges. Where better water quality is required to protect other beneficial uses of the environment in a given location, appropriate criteria and factors, including public health considerations, are taken into account.

Summary

Alkylleads have been used in Canada primarily as antiknock additives in gasoline. Tetraethyllead is the alkyllead used most commonly for this purpose. Canadian consumption of tetraethyllead in gasoline reached its peak of 16,000 tons in 1975 but has since declined dramatically with the elimination of leaded gasolines. Former secondary applications for alkylleads included their use as catalysts in the chemical industry.

Alkyllead compounds have been detected in water, sediments and biota from a large number of Ontario rivers and lakes. The greatest concentrations have occurred in the St. Lawrence River off Maitland and in the St. Clair River off Corunna, both sites of chemical production plants. In 1983, the geometric mean concentration of alkyllead compounds in water taken just below the surface off Maitland was 330 ng/L. Concentrations of alkylleads in fish from the Maitland area in 1981 had a geometric mean of 4.21 µg/g for carp, (*Cyprinus carpio*), and 0.216 µg/g for white sucker, (*Catostomus commersoni*). Total lead levels in the edible portions of a substantial number of sports fish were elevated above the provincial guidelines for unrestricted consumption (1 ppm). Alkyllead concentrations in fish and sediments at Maitland have declined significantly between 1981 and 1987 with the decrease in alkyllead production and final closure of the plant in 1985. Tetraethyllead is still produced at Corunna for use in farm machinery, aviation fuels (propeller driven aircraft) and for export.

Tetraalkylleads break down rapidly in water especially in the presence of light. Intermediate breakdown products, tri- and dialkylleads, are persistent in the aquatic environment for several months. The final breakdown product is inorganic lead.

The toxicity of the alkylleads has not been well studied because of technical problems encountered in handling these often volatile and unstable compounds. At present, sufficient

data exist for setting Provincial Water Quality Guidelines (PWQG's) for tetraethyllead, triethyllead and tetramethyllead.

The PWQG's for these organolead species are:

Species	Test Organism	Endpoint	Effect Conc. (µg/L)	Uncertainty factor	Proposed PWQG (µg/L)
tetraethyllead	trout	lethality	5	7290	0.0007
triethyllead	fish larvae	swim bladder development	90	250	0.4
tetramethyllead	trout fry	lethality	3.5	567	0.006

The PWQG for tetraethyllead is less than current detection limits in water (≈ 0.008 µg/L) using techniques available to research laboratories where small numbers of samples are involved. All of these values are lower than the current MOEE routine laboratory detection limits of 5 µg/L, 2 µg/L and 5 µg/L for tetraethyl, triethyl and tetramethyl leads, respectively. Primary chronic and acute toxicity data are required for all these chemicals in order to reduce the uncertainty factors used to derive the guidelines and to allow upgrading of these guidelines to Objectives.

Note: Concentrations in this document are expressed in a number of different units commonly used in scientific papers. The conversion factors are:

1 gram per litre (g/L) = 1000 milligrams per litre (mg/L)
1 mg/L = 1000 micrograms per litre (µg/L)
1 µg/L = 1000 nanograms per litre (ng/L)

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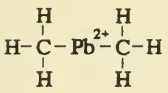
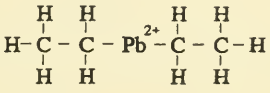
1.0 Introduction and Background

Alkylleads are organometallic compounds - compounds in which a carbon atom of one or more organic molecules is bound to a metal atom. Examples of the forms are shown below.



Dimethyllead



Diethyllead

Although some organometallic compounds form naturally, the organolead compounds found in the environment are mostly man-made. They behave as new chemicals with specific properties different from those of metallic lead (Jensen, 1984). Within each species, the number of organic molecules attached to one metal atom greatly affects the properties of organoleads. For instance, tetraalkylleads are soluble in oils and lipids but relatively insoluble in water whereas the opposite is true for their breakdown products, di- and trialkylleads (see Table 4.1). This results in higher concentrations of tetraalkylleads being found in biota and sediments, or associated with particulates and organic compounds at the water surface microlayer, but greater persistence of the di- and trialkylleads in the water column (see Section 1.2). The Ontario Ministry of Environment and Energy is setting Provincial Water Quality Guidelines for these chemicals because they have been identified as priority pollutants in a screening process based on the chemical's environmental persistence, potential to bioaccumulate, acute and sublethal toxicity to biota and potential to exist in effluents discharged to surface waters.

1.1 Sources of Alkylleads in the Aquatic Environment

Alkylleads have been detected in waters, sediments and biota from a large number of Ontario rivers and lakes (Chau *et al.* 1980; Chau *et al.* 1985; Wong *et al.* 1989). The greatest concentrations of these compounds have been found in the St. Lawrence River near Maitland and in the St. Clair River near Corunna where chemical production plants have been in operation for many years (Chau *et al.* 1985; Wong *et al.* 1988; Wong *et al.* 1989). Alkyllead concentrations in the St. Lawrence River above, below and at Maitland itself are presented in

Table 1.1 for water sampled during 1983 from just below the surface and at the surface microlayer.

Table 1.1: Alkyllead and total lead levels in water from the St. Lawrence River above and below Maitland during 1983 (Wong *et al.* 1989). All concentrations in ng/L.

Location	Sample	alkyllead		total lead	
		N[a]	geom. mean[b] (range)	N[a]	geom. mean[b] (range)
Lily Bay (15 km upstream)	subsurface[c]	1	<8	1	1740
Plant A. Maitland	subsurface	3	330 (200-470)	3	2330 (1760-2950)
	surface microlayer	3	900 (430-1910)	3	6770 (3790-9390)
Blue Church Bay (0.2 km downstream)	subsurface	3	90 (80-120)	3	1820 (1380-3140)
	surface microlayer	1	80	1	3550

[a] number of samples analyzed.

[b] Wong *et al* 1989 reported geometric means calculated from samples having alkyllead or total lead conc >8 ng/L.

[c] water samples taken just below the surface.

Alkyllead compounds in the subsurface water off Maitland had a geometric mean concentration of 330 ng/L (0.33 µg/L), while the geometric mean concentration in the surface microlayer was 900 ng/L (0.9 µg/L). The geometric mean is calculated by finding the arithmetic mean of the logarithms of the numbers, and then taking its antilogarithm (Porkess, 1988); this method is used when dealing with data that is not normally distributed. Water concentrations of alkylleads constituted 13-14% of the total lead content. Effluent quality, measured as a requirement under Municipal/Industrial Strategy for Abatement (MISA) indicated that for the organic chemical sector alkylleads in effluent discharged into the St. Clair River over a 12-month period ranged from 0.6 to 8 µg/L with a mean of 4 µg/L

(tetraalkylleads). For trialkylleads, the range was 2 to 62 µg/L with a mean of 25 µg/L (MOE 1992a).

There are two main sources of alkylleads to the aquatic environment. The primary source of these compounds results from their use as antiknock additives in gasoline. Tetraethyllead (TEL) and tetramethyllead (TML) have been used for this purpose since 1923 in the United States and 1926 in Canada (Shapiro and Frey 1968; Wong *et al.* 1989; Nriagu 1990). Before restrictions on the lead content in gasoline, few organic compounds were produced in greater quantities than alkylleads for gasoline. Peak worldwide production was about 400 x 10^3 tons Pb/year in the early 1970's (Grandjean and Nielson 1979). In Canada, consumption of TEL in gasoline declined from a peak of 16,000 tons in 1975 to 9,100 tons in 1982 (Royal Society of Canada 1986). This reduction occurred as a result of a federal standard of 0.77 g Pb/L in leaded gasoline imposed in 1974 and an increase in the number of cars designed for unleaded gasolines. In 1985, production of tetraethyllead at Maitland was halted and levels of waterborne alkyl lead have declined locally (see Section 4). As of January 1990, the sale of leaded gasoline in Canada for the domestic car market has been eliminated. Production of TEL and TML still continues at Corunna for use in farm machinery, aviation fuels (propeller driven aircraft) and for export.

Loss of TEL used in gasoline occurs during the manufacture, handling, combustion and accidental spillage of leaded gasoline. Because of its high vapour pressure, about 4 mg/L (1.3%) of TEL in gasoline is lost during the filling of storage and car tanks (Huntzicker *et al.* 1975). Older cars without antipollution devices released gasoline vapours containing TEL from the fuel tank, the carburettor and in blow-by gas from the crank case. Approximately 45% of the emission of TEL from older cars occurred from these sources (Laveskog 1971), while 1% of TEL in gasoline was released in the exhaust (Hewitt and Harrison 1986). Until restrictions were placed on the use of leaded gasoline, 1-10% of the total lead content of urban air were alkylleads originating from the automobile (Hewitt and Harrison 1986). Alkylleads from automobile exhaust are found mostly in a vapour phase with only a small fraction (< 1%) in an atmospheric aerosol (Harrison *et al.* 1985; Radojevic and Harrison 1987). The presence of diethyllead and triethyllead in the vapour phase suggests that decomposition of tetraethyllead begins in the atmosphere (Harrison *et al.* 1986a; Radojevic and Harrison 1987). Rainout/washout of atmospheric alkylleads is recognized as a major source of these compounds to surface waters (Harrison *et al.* 1986b; Radojevic and Harrison 1987). Trialkyllead concentrations in rainwater reported by Radojevic and Harrison (1987) ranged from 28 to 330 ng Pb/L. Alkylleads have been measured extensively in rainwater and

have been reported in such high concentrations (62 µg Pb/L) as to be considered responsible for damage to trees in the Black Forest, Germany (Faulstich and Stournaras 1985). With the decrease in use of leaded gasolines, the quantity of alkyllead compounds in Ontario waters from gasoline is expected to decrease considerably, although, as yet, no studies exist to confirm this.

The second source of alkylleads to the freshwater environment is from the methylation of lead in water and sediments, whether from biological or strictly chemical processes. The biological methylation of lead was first reported by Wong *et al.* (1975) who demonstrated the production of TML in anaerobic sediments from trimethyllead acetate and occasionally inorganic lead. The findings of Wong *et al.* (1975) were not supported by Jarvie *et al.* (1975) who suggested that the observed production of TML was strictly a chemical reaction (alkylation-disproportionation) involving an intermediate sulphide compound. In the same year, Schmidt and Huber (1976) reported the biologically-mediated methylation of inorganic lead in anaerobic aquarium water. They, like Jarvie *et al.* (1975), suggested that the production of TML from trimethyllead in sediments reported by Wong *et al.* (1975) was strictly a chemical reaction. In a later study, however, a biologically-mediated conversion of trimethyllead to TML was indeed confirmed (Huber *et al.* 1978). More recently, Hewitt and Harrison (1987) observed the formation of lead-210 labelled TML from estuarine sediments dosed with inorganic lead-210. A similar study on freshwater sediments, however, has not been reported. A study by Ahmad *et al.* (1980) demonstrated that synthesis of volatile TML and other tetraalkylleads from inorganic lead may also be possible in aqueous solutions.

The existence of a natural source of TML or any other alkyllead remains controversial, as well as its possible significance. While two marine studies suggest that this source may be significant (Harrison and Laxen 1978; Hewitt and Harrison 1987), no such studies exist in fresh water. Until further studies are available, the importance of naturally generated tetramethyllead remains unknown.

1.2 Fate of Alkylleads in the Aquatic Environment

The tetraalkylleads are highly volatile and relatively insoluble in water (see Appendix tables I-1, II-1, and III-1). As non-polar compounds they are associated with particulates and organic compounds in the surface microlayer (Chau *et al.* 1985; Wong *et al.* 1989). Many studies have shown that TEL and TML are unstable in freshwater and decompose in the

presence of light to di- and trialkyllead compounds. The end-product of this decomposition is inorganic lead. Break-down of TEL occurs even in the vapour state in the atmosphere before washout in rain (Harrison *et al.* 1986a; Radojevik and Harrison 1987). Grove (1980) estimated a two-day half-life for TEL in freshwater. In contrast to most studies he found that light did not appear to play an important role in decomposition. The breakdown product, triethyllead (TriEL), was very stable with a loss of only 25% observed over 60 days. Jarvie *et al.* (1981), however, observed that aqueous TEL was relatively stable in the dark (2% decomposition in 77 days) but was rapidly broken down in sunlight with only 1% of the initial TEL remaining after 15 days; the photolysis of TEL was catalyzed by cations (Fe, Cu). Tetramethyllead showed a similar pattern with a breakdown of 16% (dark) and 59% (light) of the initial amount within 22 days. The break-down product, trimethyllead (TriML), was relatively stable in light with only a 4% loss after 15 days.

Similar observations to those of Grove (1980) and Jarvie *et al.* (1981) have been made in natural rain water (Harrison *et al.* 1986a). In these experiments, using tetraalkyllead (TEL + TML) concentrations of 1-3 µg Pb/L, (about one order of magnitude greater than typically detected in rainwater), the breakdown of TEL to triethyllead was even more rapid than discussed above. Complete decomposition was observed within 48 hours even in the dark. Decomposition was accelerated by sunlight and the presence of dust particles (Harrison *et al.* 1986a; Radojevic and Harrison 1987). It is evident from these studies that tetraalkylleads will not remain for long periods of time in the freshwater environment. The trialkyllead derived from tetraalkyllead, however, will probably persist for several months as cationic compounds. Eventually these too will be degraded to inorganic lead unless a natural alkylation process is significant (see Section 1.0).

For a recent review of the fate and behaviour of alkylleads in the environment, see Rhue *et al.* (1992).

2.0 Toxicity of Alkylleads to Aquatic Organisms

The toxicity of inorganic lead to freshwater aquatic organisms has been well documented (Wong *et al.* 1978; NRCC 1978; EPA 1980; Hodson 1986). In contrast, few studies are available on the toxicity of alkylleads to freshwater organisms, despite recognition that alkylleads are much more toxic than inorganic lead because of their lipophilic nature and ability to permeate biological membranes (Hodson 1979; Grandjean and Nielsen 1979; Jensen

1984). For example, in the marine environment, the 96h LC_{50} for TML and TEL for the plaice (*Pleuronectes platessa*) were 3,600 and 700 times lower, respectively, than the LC_{50} for inorganic lead under the same conditions (Maddock and Taylor 1980). Similarly, in freshwater studies, Wong and Chau (1979) found that 20 times as much inorganic lead from lead nitrate as TML would be required to produce equivalent toxic effects on three algal species.

The paucity of toxicity studies on alkylleads can be ascribed, in part, to the chemical nature of the compounds themselves. The tetraalkylleads, including TEL and TML, are volatile, relatively insoluble and difficult to measure analytically (Shapiro and Frey 1968; Grove 1980). Analytical results in culture media can be highly variable because of the adsorption of alkylleads to suspended material and to container walls, and because of their accumulation in surface films (Grove 1980; Jarvie *et al.* 1981; Jarvie 1988; Chau *et al.* 1985 ; Wong *et al.* 1989). TEL and TML degrade rapidly in light to tri- and dialkyllead species (Grove 1980; Jarvie *et al.* 1981; Chau *et al.* 1984; Wong *et al.* 1989). Tri- and diethyllead also form complexes with the TEL parent. When complexed, these species are not freely soluble and are unavailable to test organisms (Jarvie 1988). In most studies, therefore, the concentrations of the alkyllead species in an exposure are unknown or nominal at best. In only three studies on freshwater organisms (Heumann 1987, Wong *et al.* 1981 and Wong *et al.*1987), were concentrations of the alkyllead species measured during the course of the exposures.

The degradation of TEL to tri- and diethyllead presents an unusual problem in the development of Ontario Provincial Water Quality Guidelines. Since studies suggest that TEL is considerably less persistent than its degradation product, triethyllead (see Section 1.1), a guideline for TEL may have limited meaning even when levels of this alkyllead are measured or maintained during the course of the test.

Discussion of the few available toxicity studies on the alkylleads has been divided into (1) tetraethyllead and its derivatives and (2) tetramethyllead. Guidelines have been developed for tetraethyllead, triethyllead and tetramethyllead. Insufficient data exist to develop guidelines for other alkylleads. There were also insufficient data to draw meaningful relationships between toxicity and water quality parameters such as alkalinity, pH, hardness and temperature. No toxicity data were available for freshwater invertebrates.

Comparison of toxicity studies was often complicated because of differences in the chemical species used in each test. For example, Babich and Borenfreund (1990) studied the toxic effects of triethyllead acetate and expressed their concentrations in µg Pb/L. Danil'chenko and Stroganov (1975) studied the toxicity of triethyllead chloride on fish embryo's and expressed their results in µg triethyllead chloride/L. In comparing these studies, it was assumed that there was complete dissociation of the triethyllead salt and that the anion, whether chloride or acetate, had no toxic effects at these concentrations. Concentrations were expressed in µg or mg triethyllead ion/L (µg $TriEL^+$/L). Because chemical properties are normally tabulated for specific salts and most of the information available was on the chloride species, triethyllead chloride was chosen when tabulating chemical properties of triethyllead in Table II-1.

2.1 Acute Toxicity

2.1.1 Fish

Tetraethyllead (and its degradation products: triethyllead, diethyllead)

In an early acute study, Turnbull *et al.* (1954) exposed the sunfish (*Lepomis macrochirus*) to TEL and obtained a 24 h and 48 h LC_{50} of 3.12 and 2.18 mg/L respectively. The authors observed that TEL was 3-4 times more toxic than inorganic $Pb(NO_3)$. The results of this study, however, are questionable because the experiment was conducted under static conditions, concentrations were nominal and the toxic concentrations were an order of magnitude greater than the reported solubility of TEL in fresh water (0.2 mg/L).

Wong *et al.* (1987) exposed yearling rainbow trout to TEL in bioaccumulation studies. While all control fish and fish exposed to 2.5 µg/L TEL survived the three week experiment, fish exposed to 10 and 5 µg/L TEL had median lethal times (LT_{50}'s) of 9 and 15 days, respectively. These data were considered acute due to the large size of the fish in the experiment.

In a tissue culture study, Babich and Borenfreund (1990) determined the toxicity of di- and trialkyllead compounds to cultures of epithelioid cells from the fin tissues of the bluegill sunfish (*Lepomis macrochirus*). However, since this assay was conducted on isolated epithelioid cells, the results cannot be related directly to the detrimental effects of trialkyllead on the whole sunfish and therefore cannot be used in guideline development.

Tetramethyllead

Only one acute study was available on freshwater fish exposed to TML. Wong *et al.* (1981), using a continuous flow system, exposed rainbow trout fingerlings to a constant level of TML as determined by daily monitoring. The study was designed primarily as an accumulation-depuration experiment. Twenty gram fish exhibited 20% mortality at 24 µg/L and 67% mortality at 51 µg/L after 10 day exposures. The toxicity data from this study cannot be regarded as primary, despite the daily monitoring, because of the lack of replication and statistical treatment of the data.

2.2 Chronic Toxicity

2.2.1 Fish

Tetraethyllead (and its degradation products: triethyllead, diethyllead)

No chronic studies were available on the toxicity of tetraethyllead (TEL) to fish.

The most detailed study on the chronic effects of triethyllead on fish is that of Danil'chenko and Stroganov (1975) who exposed the embryos and larvae of pike (*Esox lucius*), perch (*Perca fluviatilis*), ruffe (*Acerina cernua*), roach (*Rutilus*), minnow (*Phoxinus phoxinus*) and the gudgeon (*Gobio gobio*) to triethyllead chloride. At 5 mg/L (4.5 mg $TriEL^+$/L) and 0.5 mg/L (0.45 mg $TriEL^+$/L) embryonic development of all test species was either arrested completely or the resulting larvae displayed significant terata. At 0.1 mg/L (0.09 mg $TriEL^+$/L), most species (minnow, roach, gudgeon, perch) were able to form larvae but these showed distinct morphological deviations from controls. In the roach and the gudgeon, inflation of the swim bladder either did not take place or was delayed. Concentrations of triethyllead chloride in this study were only nominal and exposure times were not presented.

Tetramethyllead

The Wong *et al.* (1981) study on TML provided chronic data as well as the acute data described previously (section 2.1.1). Mortality was 17% during exposure of thirty 1 g rainbow trout fry for 14 days to 3.5 µg/L in a continuous flow, accumulation-depuration study. As in the acute tests, the toxicity data from this study cannot be regarded as primary,

despite daily monitoring of the TML concentration, because of the lack of replication and statistical treatment of the data.

2.2.2 Algae/Aquatic Plants

Tetraethyllead (and its degradation products: triethyllead, diethyllead)

In a series of related studies, Roderer (1980, 1981, 1984, 1986, 1987) examined the toxicity of tetraethyllead and triethyllead to the freshwater alga *Poteriochromanas malhamensis*. Cultures exposed to 3.2-97 mg/L TEL in the dark for 72 h demonstrated no toxic effects relative to controls. In the presence of light, however, growth of *P. malhamensis* was inhibited at TEL concentrations of 3.2-16.2 mg/L and abnormal development was observed in the cell nuclei. At 80 mg/L no cells survived. Toxic effects increased with the length of exposure to light and decreased with aeration of the culture medium. Roderer concluded that TEL was relatively nontoxic but degraded to a toxic triethyllead in the presence of light. Separate tests using triethyllead chloride in the dark supported his conclusions as similar toxic effects to TEL in light were observed at 1.65-8.24 mg/L (1:47-7.35 mg $TriEL^+$/L). Higher concentrations of triethyllead were lethal. Diethyllead (as diethyllead dichloride) was less toxic than triethyllead but produced similar effects at 8.40-33.6 mg/L in the dark. In the presence of light, diethyllead was observed to decompose to an unidentified inorganic form precipitating on the walls of the exposure vessel.

Roderer's explanation of the role of light in the toxicity of TEL (Roderer 1980) has been corroborated by Jarvie *et al.* (1981) and Jarvie (1988) who examined the photodegradation of TEL in water. Roderer's toxicity levels for TEL, however, must be questioned because these concentrations of TEL are well above its reported solubility in water and the actual concentrations of the breakdown product, triethyllead, are unknown. More confidence can be placed in the separate toxicity value for triethyllead.

In a study by Heumann (1987), *Chara vulgaris* exposed to triethyllead chloride for 14 days exhibited a 50% inhibition in growth at 0.53 mg/L (0.47 mg $TriEL^+$/L). A concentration of 2.5 mg/L (2.2 mg $TriEL^+$/L) was lethal to this macrophytic alga within seven days. Ultrastructural effects were evident in *Chara* at concentrations of 0.82 mg/L (0.73 mg $TriEL^+$/L). These included alterations to the membrane systems of the chloroplasts.

Tetramethyllead (and its degradation product: trimethyllead)

Effects of TML and its degradation product (trimethyllead) on algae are qualitatively similar to those of TEL and its derivatives. In a study of TML on three algal species (*Scenedesmus quadricauda*, *Ankistrodesmus falcatus* and *Chlorella pyrenoidosa*), Silverberg *et al.*(1977) observed a 32-74% reduction of growth relative to controls (see also Chau and Wong 1980). Photosynthesis, as determined by the C^{14} method, was reduced by 49-85%. Additional effects included a large variety of cytological abnormalities. The TML was generated biologically from Hamilton Harbour sediments and was bubbled into a flask containing the test algae in culture medium. Exposures to the relatively insoluble TML were momentary and the authors estimated that less than 0.5 mg of lead as TML passed through the culture medium. Based on the volume of their culture medium (1500mL), the algae were exposed to a maximum concentration of about 430 µg/L TML. While not exceeding the solubility of TML in water, this concentration was not analytically confirmed and the exposure time was also unclear.

In studies of trimethyllead on *P. malhamensis*, Roderer (1984) observed a similar inhibition of growth and a range of cytological abnormalities over an effective concentration range of 0.71-8.6 mg/L. Above 8.6 mg/L trimethyllead was lethal to the alga.

2.3 Summary of Toxicity Data

The following is a brief summary of the toxicity studies available for TEL, triethyllead and TML relevant to setting Ontario Provincial Water Quality Guidelines.

Tetraethyllead

The most sensitive species was rainbow trout exposed as 300g juveniles to 5 µg/L TEL and exhibiting an LT_{50} of 15 days. The NOEC (21d) was 2.5 µg/L (Wong *et al.* 1987). A 48 h LC_{50} of 2.18 mg/L was observed for the sunfish *Lepomis macrochirus* (Turnbull *et al.* 1954). The alga, *Poteriochromonas malhamensis* was considerably less sensitive than trout and exhibited growth inhibition and cytological abnormalities at 3.2 mg/L (Roderer 1980).

Triethyllead

The most sensitive fish species were the roach and gudgeon exposed as embryos and larvae to 0.1 mg/L triethyllead chloride (90 µg $TriEL^+$/L) and exhibiting morphological changes and changes to the functioning of the swim bladder. The minnow, ruffe and pike were slightly less sensitive to TriEL. A concentration of 0.45 mg $TriEL^+$/L was lethal to embryos of the minnow, while 0.90 mg $TriEL^+$/L caused morphological changes to ruffe and pike larvae (Danil'chenko and Stroganov 1975). Algae appeared to be much less sensitive to TEL and its degradation products. Growth of the alga *Poteriochromanas malhamensis* was inhibited at 1.65 mg/L triethyllead chloride (1.47 mg $TriEL^+$/L; Roderer 1981) and *Chara vulgaris* at 0.53 mg/L (0.47 mg $TriEL^+$/L; Heumann 1987).

Tetramethyllead

The only data on the toxicity of TML to fish are from bioconcentration studies by Wong *et al.* (1981). At 24 µg/L, 20% acute lethality was observed in rainbow trout fingerlings. In chronic exposures at 3.5 µg/L, 17% lethality was observed in rainbow trout fry. As with TEL, algae were less sensitive to TML than fish. In *Scenedesmus* spp., *Ankistrodesmus* spp. and *Chlorella* spp. growth was reduced at a calculated concentration of 0.43 mg/L (Silverberg *et al.* 1977).

Trimethyllead

Roderer (1984) observed an inhibition of growth in *Poteriochromanas malhamensis* at 0.71 mg/L TriML.

3.0 Mutagenicity and Carcinogenicity

Little data are available pertaining to the mutagenic properties of the alkylleads. The U.S. EPA has not evaluated tetraethyllead for evidence of human carcinogenic potential (IRIS 1992). A study by Epstein and Mantel (1968) reported a higher incidence of lymphomas in female mice after exposure to TEL, however these tumours were known to occur spontaneously in the strain of mouse used (IARC 1973). Although Robinson (1974) reported no increase in the cancer rate during a 20 year follow-up of workers exposed to TEL, Haring (1981) reported that three workers in a TEL production plant developed multiple myelomas, thirty times more than expected. McClain and Becker (1972) report that

experiments with rats indicate that TEL is essentially non-teratogenic. Kennedy et al. (1975) report that tetraethyllead did not promote a dominant lethal effect in mice for mutagenic effects upon developing germinal cells in male mice. One study was found indicating a positive result in a cell transformation assay using Syrian hamster embryo cells (IRIS 1992), however this may not indicate that TEL is genotoxic (D. Rokosh, pers. comm. Standards Development Branch, MOEE). The one Ames test found was negative for mutagenic effects. Thus, weight of evidence suggests that TEL is non-genotoxic, non-mutagenic, non-teratogenic and possibly a weak carcinogen.

No data were found on the teratogenic properties of triethyllead. IARC could not classify the carcinogenicity of triethyllead due to lack of data (IRIS 1992). Odenbro and Kihlstrom (1977) reported no evidence of teratogenic effects in mice exposed to maximally tolerated doses of triethyllead. An increased occurrence of chromosome nondisjunction has been observed in *Drosophila melanogaster* when larvae were exposed to triethyllead chloride (Ahlberg *et al.* 1972). Furthermore, Ahlberg *et al.* (1972) reported that an increased occurrence of chromatid breakage occurred when fly larvae were exposed to triethyllead chloride. Danil'chenko and Stroganov (1975) reported that fish exposed to triethyllead chloride exhibited morphological disorders such as incomplete development of organs, tail curvature and distortion of the vertebral columns. These effects indicate that triethyllead may be a teratogen and a mutagen.

No data were found relating to the teratogenic, mutagenic or carcinogenic properties of trimethyllead. IRIS (1992) reports no mutagenic response was obtained in *Salmonella typhimurium* exposed to tetramethyllead. However there are insufficient data to make a decision on the genotoxic effects of tetramethyllead.

In comparison, there is sufficient animal evidence to show that inorganic lead salts are carcinogenic. It has been classed as a probable human carcinogen by the U.S. EPA (IRIS 1992). Long term dietary and subcutaneous exposure result in a significant increase in renal tumours. Short term studies show that lead affects gene expression. Lead acetate induced cell transformation in Syrian hamster embryo cells and also enhanced the incidence of simian adenovirus induction. Lead oxide showed similar enhanced adenovirus induction (from IRIS 1992). Lead compounds were also shown to be capable of inducing chromosomal aberrations *in vivo* and in tissue cultures (from IRIS 1992).

Whether the alkylation of lead would increase or decrease the possibility to cause genotoxic damage is uncertain. Since there are no studies available on the genotoxic effects of the alkylleads to aquatic organisms the mutagenicity component of the PWQG cannot be incorporated. At present, only sufficient information for tetraethyllead and triethyllead are available for narrative mutagenicity guidelines. Tetraethyllead is not expected to cause mutagenic effects in aquatic organisms. There is evidence suggesting that triethyllead is clastogenic (results in chromosomal damage) in insects and may result in teratogenic effects to fish. However, there are insufficient data to produce a guideline value based on mutagenicity for triethyllead. Insufficient information exists to classify the remaining compounds with regards to mutagenic effects.

4.0 Bioaccumulation

The accumulation of alkyllead compounds in freshwater organisms is dependent on their lipophilic nature, often expressed as an octanol/water partition coefficient. Since there are no direct measurements of octanol/water partition coefficients reported for the alkylleads, values were estimated from an empirical relation between water solubility and log K_{ow} published by Chiou *et al.* (1977). These estimates (Table 4.1) suggest that only tetraethyllead (log K_{ow} = 5.1) and, marginally, tetramethyllead (log K_{ow} = 3.7), are sufficiently non-polar and lipophilic to accumulate significantly in the fatty tissues of aquatic organisms. The ionic degradation products (di- and triethyllead) are quite soluble in water and are not expected to accumulate significantly in aquatic biota. These species are actually more soluble in water than inorganic lead chloride (Table 4.1).

Table 4.1: Water Solubility of Lead Species and Calculated[1] Octanol - Water Partition Coefficients for Alkylleads.

Parameter	Water Solubility[2] (µmoles/L)	log K_{ow}
Tetraethlylead	0.62	5.1
Triethyllead chloride	6.1×10^4	1.8
Diethyllead dichloride	1.5×10^5	1.5
Tetramethyllead	67	3.7
Lead chloride ($PbCl_2$)	3.6×10^4	--

[1] as calculated from Chiou *et al.* (1977)
[2] as reported in Jensen (1984), 25°C

Results from field and laboratory studies support the conclusion that fish accumulate lipophilic tetramethyllead (TML) and tetraethyllead (TEL) more readily than inorganic lead. Exposure of rainbow trout to 3.5 µg/L TML resulted in whole body lead concentrations of 2.54 µg/g (wet weight) after seven days exposure (Wong *et al.* 1981). Trout exposed to lead nitrate under similar conditions contained equivalent lead concentrations when water concentrations were 50-60 µg/L (Hodson 1979). Tetraalkylleads accumulated preferentially in the fatty tissues of the intestine (Wong *et al.* 1988; 1989). Analysis of the alkyllead species in a variety of fish exposed to TEL in the St. Lawrence River (see below) indicated that the majority was in the form of tetraethyllead and its degradation products (Wong *et al.* 1989). The occurrence of these degradation products was attributed to metabolic dealkylation of the TEL in the fish.

Very few field studies of alkylleads in freshwater organisms have been conducted. Most of the information available comes from Canadian studies on the St. Lawrence and St. Clair Rivers (Chau *et al.* 1984; Chau *et al.* 1985; Wong *et al.* 1988; Wong *et al.* 1989; Scheider *et al.* 1986; MOE, unpublished data). Alkylleads in these locations were derived largely from two chemical plants, Dupont Canada at Maitland (St. Lawrence River) and Ethyl Canada in Corunna (St. Clair River). Levels of alkylleads in fish were substantially elevated near these industries with TEL and triethyllead as the predominant species. Total lead levels in the edible portions of a substantial number of sport fish from Blue Church Bay off Maitland were higher than the 1.0 ppm Health and Welfare number for unrestricted consumption (Scheider *et al.* 1986; MOE, unpublished data). Most fish from the contaminated area at Maitland contained approximately 50-75 percent of their total lead as alkylleads (Wong *et al.* 1988, Wong *et al.* 1989). One carp downstream of Maitland contained 139 µg/g alkyllead (whole fish minus intestine, wet weight), a value representing the highest concentration of lead (organic or inorganic) ever reported in fish. For comparison, a study of total lead in fish from the Great Lakes showed residues normally less than 0.1 µg/g and maximum values rarely exceeded 0.5 µg/g (whole body, wet weight)(Hodson *et al.* 1984).

Concentration of alkylleads at Maitland varied between fish species. Yellow perch, carp, smallmouth bass and white sucker had higher alkyllead concentrations than pike, alewife and rock bass (Table 4.2). Differences between species were attributable to differences in feeding habits, lipid content of the fish and location of capture. In most species, the greatest concentrations of alkylleads were found in the fatty intestinal tissues of the fish (Table 4.2).

Analysis of fish samples from the Maitland area between 1981 and 1987 indicated that levels of alkylleads were highest in 1981, with geometric means of 4.207 µg/g (4207 ng/g) for carp and 0.218 µg/g (218 ng/g) for white sucker (Wong *et al.* 1989). Since 1981, alkyllead concentrations in fish have declined significantly, reflecting reductions in effluent discharge and closure of the source in 1985. In 1987, the geometric mean alkyllead concentration for all fish was less than 0.150 µg/g. A similar reduction in total lead concentrations was also observed over the same period of time (MOE, unpublished data).

Table 4.2. Concentrations of alkylleads (ng/g wet weight) in whole fish (minus intestine) and fish intestine from the St. Lawrence River near Maitland, Ontario during 1981 and 1982 (Wong *et al.* 1989).

Fish species	Whole fish minus intestine			Intestine only		
	N[a]	geom. mean[b]	range	N	geom. mean	range
1981 data						
Carp	12	4207	190-138999	12	2919	100-100644
White sucker	10	218	24-1221	10	1009	236-3447
Northern pike	6	173	30-1384	6	2248	1360-4454
1982 data						
Yellow perch	5	1994	912-5415			
Carp	5	1976	102-61713	6	1606	159-30608
Smallmouth bass	4	1972	890-3115	3	3198	1955-5079
White sucker	3	1747	171-3187	3	6336	2767-12085
Brown bullhead	2	1135	553-2329	2	587	328-1052
Redhorse sucker	5	721	189-2042	5	1486	350-4857
Pumpkinseed	5	567	89-1882			
Pike	4	287	55-1324	5	981	411-2063
Alewife	2	244	209-285			

[a] number of fish in sample.
[b] tissue concentrations expressed as the geometric mean.

Very few bioconcentration factors have been calculated for the alkylleads. A single whole-organism bioconcentration factor (BCF) is available for TML from the laboratory study of Wong *et al.* (1981). A BCF of 726 was determined for rainbow trout fry (1g) exposed to

3.5 µg TML/L (as Pb) for a period of one week. Analysis of tissues from 300g rainbow trout exposed for 3 weeks to 2.5 µg/L TEL showed bioconcentration factors of 3189 (visceral fats), 1824 (intestine), 1500 (skin), and 834 (kidney). However, whole fish bioconcentration factors were not measured.

In laboratory tests with lower trophic levels using trialkylleads, bioconcentration of TriML was greater than TriEL in muscle (adductor muscle and foot), gill, mantle, and visceral mass tissues of adult freshwater mussels, *Elliptio complanata*, 6-7 mm in length. After 14 d exposures to 1 mg/L TriML and TriEL, the highest wet weight tissue concentration for TriML was 19.7 µg/g in muscle tissue and for TriEL was 5.9 µg/g in muscle and in visceral mass tissues. Bioconcentration factors were 8-fold and 3-fold respectively.

5.0 Derivation of the Water Quality Guidelines

The uncertainty factors and Provincial Water Quality Guidelines (PWQG's) were developed according to the procedures specified by the Ontario Ministry of the Environment (MOE 1992b) and can be found in detail in Appendices I-III. A list of references used for the guideline development is shown in Appendix IV. As shown in Table 3 of each of the appendices, the final uncertainty factor applied to the lowest toxicity value depends on the quantity and quality of available data. Hence, guidelines for related chemicals do not necessarily have similar values. Nor do the values bear any relationship to what might be expected on the basis of QSAR. Separate guidelines were developed for tetraethyllead (TEL), triethyllead (TriEL) and tetramethyllead (TML). Insufficient data exist for using bioaccumulation and impacts on taste and odour in calculating the guidelines. Because of high uncertainty factors the guidelines for TEL and TML are very low. In fact, the guideline for TEL is less than typical analytical detection limits such as those obtained at the National Water Research Institute of Environment Canada (i.e. 8 ng/L; Chau *et al.* 1985). All three guidelines are below the MOEE Laboratory Services Branch routine detection limits (5 µg/L, 2 µg/L, and 5 µg/L for TEL, TriEL, and TML, respectively).

Tetraethyllead

The acute toxicity data from the accumulation-depuration study of Wong *et al.* (1987) on rainbow trout were considered secondary, even though a flow-through system was used and test concentrations were measured, because there was no replication and therefore no

statistical analysis of the data. The calibration factor was therefore assigned a value of 0.9. As in all algal studies where exposures are long relative to life cycles and the effects of the growth medium on toxicity are unknown, the study on *P. malhamensis* by Roderer (1980) was considered as chronic and secondary (calibration factor = 0.9). The acute study by Turnbull (1954) on the sunfish was also secondary since the experiment was static with nominal concentrations (calibration factor = 0.9). Since the log K_{ow} for TEL was calculated as 5.1, the baseline uncertainty factor is 10,000 and the final uncertainty factor 7290. The critical value for guideline development was taken as 5 µg/L from the rainbow trout study (Wong *et al.* 1987). The recommended final PWQG is therefore 0.0007 µg/L.

Triethyllead

The chronic study of Danil'chenko and Stroganov (1975) was considered secondary because of nominal concentrations and unspecified exposure times. Three warm-water fish species from this study were assigned calibration factors of 0.7 and two of these chronic studies were substituted for acute toxicity data with calibration factors of 0.9. The algal study by Heumann (1987) was assigned a calibration factor of 0.9. Since the log K_{ow} for triethyllead chloride was calculated as 1.8, a baseline uncertainty factor of 1000 was adopted and a final uncertainty factor calculated as 250. The critical value for guideline development was taken as 90 µg triethyllead ion/L from the chronic study by Danil'chenko and Stroganov (1975) on the larvae of roach and gudgeon in which abnormal development of the swim bladder was observed. The recommended final PWQG is therefore 0.4 µg/L.

Tetramethyllead

The toxicity data from bioaccumulation studies on rainbow trout by Wong *et al.* (1981) were considered secondary because of the lack of replication and statistical treatment of the data. The chronic study on fry and the acute study on fingerlings were assigned calibration factors of 0.7 and 0.9 respectively. As with all algal studies, the algal study by Silverberg *et al.* (1977) was also considered as secondary (calibration factor = 0.9). The log K_{ow} for TML was calculated as 3.7, therefore a baseline uncertainty factor of 1,000 was adopted. The final uncertainty factor was calculated to be 567. The critical value for guideline development was taken as 3.5 µg/L from the study of Wong *et al.* (1981). The recommended final PWQG is therefore 0.006 µg/L.

Trimethyllead

The only freshwater studies using trimethyllead (TriML) are the algal toxicity study reported by Roderer, (1984), and the mussel tissue bioaccumulation study by Chau *et al.*, (1988). Ontario Provincial Water Quality Objectives and Guidelines cannot be set on these studies alone (MOE, 1992).

6.0 Research Needs

There is an evident need for further research into the toxicity of the alkylleads to freshwater organisms. The studies available were few and of secondary data quality. The final uncertainty factors were large and consequently the guidelines developed for tetraethyllead and tetramethyllead were very low, in fact, that for tetraethyllead is below analytical detection limits. Research is required in the following areas to lower uncertainty factors and promote development of Objectives from Guidelines:

(1) Additional toxicity studies yielding primary data are required. Only secondary data were available on fish and there were no data on invertebrates.
(2) The potential for water quality parameters (pH, alkalinity, hardness, temperature, etc.) to affect the toxicity of these compounds needs to be evaluated.
(3) Laboratory studies are required on bioaccumulation of alkylleads in whole freshwater organisms.
(4) Measured log K_{ow} values are needed for all alkylleads, especially tetramethyllead (TML) and tetraethyllead (TEL).
(5) The role of natural alkylation as a source of alkylleads should be clarified.
(6) There is also a recommendation that current routine analytical detection limits for the alkylleads should be lowered.

7.0 Objectives of Other Agencies

No water quality guidelines or objectives of other agencies were available for comparison with the guidelines developed in this document. Tetraethyllead is one of the

"Group A" substances on the secondary list of chemicals proposed for bans and phase-outs by the Ontario Ministry of the Environment and Energy (MOE 1992c).

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Appendix I: Tables for Derivation of Provincial Water Quality Guidelines for Tetraethyllead (See Appendix IV for numbered references.)

Table I-1: Physical-chemical properties for tetraethlylead (References in Parentheses given in Appendix IV)

TABLE I-1: PHYSICAL-CHEMICAL PROPERTIES		
COMPOUND:	**CHEMICAL FORMULA:**	**CAS No.:**
Tetraethyllead (TEL)	$Pb(C_2H_5)_4$	78-00-2

PROPERTIES	
MOLECULAR WEIGHT (MW):	323.20 g/mol
MELTING POINT:	-136°C (1)
BOILING POINT:	198 - 202°C (2)
PHYSICAL STATE AT ROOM TEMP.:	liquid
DISSOCIATION CONSTANT (pKa):	non-polar
LIQUID DENSITY (D):	1.65 g/cm^3 @ 20°C (1)
MOLAR VOLUME (MW/D):	195.6 cm^3/mol (2)
VAPOUR PRESSURE (P^s):	33.7 Pa @ 20°C (= 0.253 mm Hg) (2)
WATER SOLUBILITY (C^s):	6.2 x 10^{-4} mol/m^3 @ 25°C (= 0.2 mg/L) (2)
HENRY'S LAW (P^s/C^s):	5.4 x 10^4 Pa· m^3/mol (calculated)

OCTANOL-WATER PARTITION COEFFICIENT (K_{ow})	
AVAILABLE Log K_{ow} VALUES:	5.1 (calculated - ref 4)
FINAL CHOSEN Log K_{ow} VALUE:	5.1

BASELINE UNCERTAINTY FACTOR FOR GUIDELINE DEVELOPMENT		
IF valid log K_{ow} < 4.0, use 1000		
IF valid log K_{ow} ≥ 4.0, use 10 000		
BASELINE UNCERTAINTY FACTOR:	10 000	ENTERED ON TABLE I-3

Table I–2: AQUATIC TOXICITY DATA TABLE FOR TETRAETHYLLEAD

Species	Life Stage	Response Key (1)	Test Solution Parameters					Effect Conc. (ug/L)	Data Codes Key (2)	Ref. No.	Data Quality Key (3)
			pH	Temp. °C	D.O. (mg/L)	Hardness (mg/L CaCO3)	Alkalinity (mg/L CaCO3)				
VERTEBRATES											
Bluegill		24h LC50	6.9-7.5	20		89.0-163	33.0-81	3120	SU	6	SA
		48h LC50	6.9-7.5	20		89.0-163	33.0-81	2180	SU	6	SA
Rainbow trout	300 g	15d LT50						5	FU	5	SA
	300 g	9d LT50						10	FU	5	SA
	300 g	21d NOEC						2.5	FU	5	SA
ALGAE											
Poterlochromanus malhamensis		72h growth inhibition & cytological abnorm.		27	Culture medium Light Intensity of 18000 lux			3200	SU	7	SC

Key (1)	Key (2)	Key (3)
TLm = Median Tolerance Limit LC = Lethal Concentration IC = Immobilization Concentration EC = Effects Concentration LT50 = Median Lethal Time NOEC = No Observed Effect Concentration	S = static R = static with renewal F = flowthrough U = unmeasured toxicant concentration M = measured toxicant concentration	P = Primary S = Secondary A = Acute Toxicity C = Chronic Toxicity

Table I-3: UNCERTAINTY FACTOR WORKSHEET

CHEMICAL:	CAS No.	CONCENTRATION UNITS
Tetraethyllead	78-00-2	ug/L

Test Conditions		Species (life stage)	Toxicity End Point	Effect conc.	Data Codes [1]	Data Type [2]	Calibration Factor	No. and Reference
ACUTE	VERTEBRATE	Bluegill sunfish	48h-LC50	2180	SU	2°	0.9	Turnbull et al. 1984 (6)
		Rainbow trout	15d-LT50	5	FU	2°	0.9	Wong et al. 1987 (5)
	INVERT.							
CHRONIC	VERTEBRATE							
	INVERT.							
	PLANT	*P. malhamensis*	72h-gr. inhib. cyt. abnorm.	3200	SU	2°	0.9	Roderer 1990 (7)

CALCULATION OF FINAL UNCERTAINTY FACTOR:

Since Log Kow > 4.00, The Baseline Uncertainty Factor = 10000

Baseline Uncertainty Factor X Calibration Factors (maximum number = 11)

10000 X .9 X .9 X .9 X [ ] X [ ] X [ ] X [ ] X [ ] X [ ] X [ ] X [ ]

= 7290 FINAL UNCERTAINTY FACTOR (NOT TO BE LESS THAN A VALUE OF 13)

CRITICAL VALUE ÷ FINAL UNCERTAINTY FACTOR = PWQG OR INTERIM GUIDELINE VALUE

= 5 ÷ 7290 = 0.0007 ug/L

[1] Assign 2 DATA CODES, one from each of the following rows:
C = chronic A = acute
S = static R = static/renewal F = flowthrough
U = unmeasured nominal conc. M = measured conc

[2] DATA TYPE:
1° = Primary 2° = Secondary 3° = Simulated Data
? = Unknown (Default Data Quality = 2°)

FIG. I-1: GUIDELINE DERIVATION GRAPH - TETRAETHYLLEAD

Toxicity Information Considered		Species and Life Stage	Exposure and Duration	Concentration (ug/L)	Ref. No.
ACUTE	Vert.	Bluegill	24h LC50	■	6
			48h LC50	■	6
		Rainbow trout (yearling)	9d LT50	■	5
			21d NOEC exposure	□	5
			15d LT50	○	5
CHRONIC	Plant	*Poterlochromanus malhamensis*	72 h exposure caused growth inhibition, cytological abnormalities	■	7
taste odour tainting		N.A.			
BCF		N.A.			
PWQG		Based on critical value of 5 ug/L and Final Uncertainty Factor of 7290	0.0007ug/L	*	
Other Agency Objectives			N.A.		

0.00001 0.0001 0.001 0.01 0.1 1 10 100 1000 10000

○ - Critical Value ■ - Toxicity endpoints ▲ - Objectives of other agencies
* - Advisory/PWQG △ - Odour Protection Values □ - No effect concentrations

Appendix II: Tables for Derivation of Provincial Water Quality Guidelines for Triethyllead (See Appendix IV for numbered references.)

Table II-1: Physical-chemical properties for triethyllead (References in Parentheses given in Appendix IV)

TABLE II-1: PHYSICAL-CHEMICAL PROPERTIES		
COMPOUND:	**CHEMICAL FORMULA:**	**CAS No.:**
Triethyllead (TriEL)	**Triethyllead chloride** $(C_2H_5)_3PbCl$	1067-14-7

PROPERTIES	
MOLECULAR WEIGHT (MW):	329.7 g/mol
MELTING POINT:	decomposes at 120°C (1)
BOILING POINT:	N.A.
PHYSICAL STATE AT ROOM TEMP.:	solid
DISSOCIATION CONSTANT (pKa):	-9.1 (13)
LIQUID DENSITY (D):	N.A.
MOLAR VOLUME (MW/D):	N.A.
VAPOUR PRESSURE (P^s):	N.A.
WATER SOLUBILITY (C^s):	61 mol/m^3 @ 25°C (= 20.1 g/L) (2)
HENRY'S LAW (P^s/C^s):	N.A.

OCTANOL-WATER PARTITION COEFFICIENT (K_{ow})	
AVAILABLE Log K_{ow} VALUES:	1.8 (calculated - ref 4)
FINAL CHOSEN Log K_{ow} VALUE:	1.8

BASELINE UNCERTAINTY FACTOR FOR GUIDELINE DEVELOPMENT		
IF valid log K_{ow} < 4.0, use 1000		
IF valid log K_{ow} ≥ 4.0, use 10 000		
BASELINE UNCERTAINTY FACTOR:	1000	ENTERED ON TABLE II-3

Table II-2: AQUATIC TOXICITY DATA TABLE FOR TRIETHYLLEAD

Species	Life Stage	Response Key (1)	Test Solution Parameters pH	Temp. °C	D.O. (mg/L)	Hardness (mg/L as CaCO3)	Alkalinity (mg/L as CaCO3)	Effect Conc. (ug/L)	Data Codes Key (2)	Ref. No.	Data Quality Key (3)
VERTEBRATES											
Pike	embryo	* caused 100% prolarval death						4500	SU	10	SC
Esox lucius	larval	* fish exhibited extensive deformities						900	SU	10	SC
Perch	embryo	* caused 100% prolarval death						4500	SU	10	SC
Perca fluvatilis											
Ruffe	embryo	* caused 100% prolarval death						4500	SU	10	SC
Acerina cernua	larval	* fish exhibited extensive deformities						900	SU	10	SC
Roach	embryo	* caused 100% prolarval death						450	SU	10	SC
Rutilus rutilus	larval	* fish exhibited extensive deformities						90	SU	10	SC
Minnow	embryo	* caused 100% prolarval death						450	SU	10	SC
Phoxinus phoxinus											
Gudgeon	embryo	* caused 100% prolarval death						4500	SU	10	SC
Gobio gobio	larval	* fish exhibited extensive deformities						90	SU	10	SC
ALGAE											
Poteriochromanus malhamensis		72h growth inhibition polyploidy			Culture Medium (Bactotryptone)			1470	SU	11	SC
Chara vulgarus		14d EC50 growth inhibition		20	Culture Medium (Forsberg)			470	SM	12	SC
		ultrastructural effects		20	Culture Medium (Forsberg)			730	SM	12	SC

Key (1)	Key (2)	Key (3)
TLm = Median Tolerance Limit LC = Lethal Concentration IC = Immobilization Concentration EC = Effects Concentration LT50 = Median Lethal Time NOEC = No Observed Effect Concentration * = Exposure Time Not Given hist = Histological Effects Observed	S = Static R = Renewed Static F = Flowthrough U = Unmeasured Toxicant Concentration M = Measured Toxicant Concentration	P = Primary S = Secondary A = Acute Toxicity C = Chronic Toxicity

Table II-3: UNCERTAINTY FACTOR WORKSHEET

CHEMICAL:	CAS No.	CONCENTRATION UNITS
Triethyllead	1067-14-7	ug/L

Test Conditions		Species (life stage)	Toxicity End Point	Effect conc.	Data[1] Codes	Data[2] Type	Calibration Factor	No. and Reference
ACUTE	VERTEBRATE	Pike, larvae	Histol.	900	SU	2°	0.9	Danil'chenko & Stroganov, 1975 (10)
		Ruffe, larvae	Histol.	900	SU	2°	0.9	Danil'chenko & Stroganov, 1975 (10)
	INVERT.							
CHRONIC	VERTEBRATE	Roach, larvae	Histol.	90	SU	2°	0.7	Danil'chenko & Stroganov, 1975 (10)
		Gudgeon, larvae	Histol.	90	SU	2°	0.7	Danil'chenko & Stroganov, 1975 (10)
		Minnow, embryo	Lethal conc.	450	SU	2°	0.7	Danil'chenko & Stroganov, 1975 (10)
	INVERT.							
	PLANT	*Chara vulgaris*	14d-EC50 (growth)	470	SM	2°	0.9	Heumann 1987 (12)

CALCULATION OF FINAL UNCERTAINTY FACTOR:

Since Log Kow < 4.00, The Baseline Uncertainty Factor = 1000

Baseline Uncertainty Factor X Calibration Factors (maximum number = 11)

1000 X .7 X .7 X .7 X .9 X .9 X .9 X ___ X ___ X ___ X ___ X ___

= 250 FINAL UNCERTAINTY FACTOR (NOT TO BE LESS THAN A VALUE OF 13)

CRITICAL VALUE ÷ FINAL UNCERTAINTY FACTOR = PWQG OR INTERIM GUIDELINE VALUE

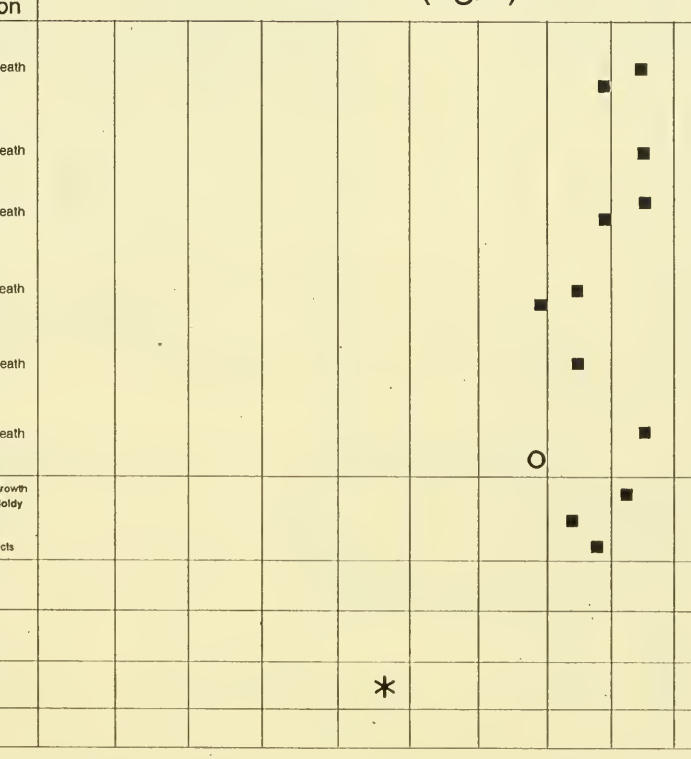
= 90 ÷ 250 = 0.4 ug/L

[1] Assign 2 DATA CODES, one from each of the following rows:
C = chronic A = acute
S = static R = static/renewal F = flowthrough
U = unmeasured nominal conc. M = measured conc

[2] DATA TYPE:
1° = Primary 2° = Secondary 3° = Simulated Data
? = Unknown (Default Data Quality = 2°)

FIG. II-1: GUIDELINE DERIVATION GRAPH - TRIETHYLLEAD

Toxicity Information Considered		Species and Life Stage	Exposure and Duration	Ref. No.
CHRONIC	Vert.	Pike		
		embryo	* - Prolarval death	10
		larvae	* deformities	10
		Perch		
		embryo	* - Prolarval death	10
		Ruffe		
		embryo	* - Prolarval death	10
		larvae	* deformities	10
		Roach		
		embryo	* - Prolarval death	10
		larvae	* deformities	10
		minnow		
		embryo	* - Prolarval death	10
		Gudgeon		
		embryo	* - Prolarval death	10
		larvae	* deformities	10
	Plant	*Poteriochromanus malhamensis*	72 h exposure - growth inhibition, polyploidy	11
		Chara vulgaris	14d EC50 growth inhibition ultrastructural effects	12 12
taste odour tainting				
BCF		N A		
PWQG		Based on critical value of 90 ug/L and Final Uncertainty Factor of 250	0.4ug/L	
Other Agency Objectives			N A	



o - Critical Value ■ - Toxicity endpoints ▲- Objectives of other agencies
✳-Advisory/PWQG △- Odour Protection Values * - Exposure Times Not Given

Appendix III: Tables for Derivation of Provincial Water Quality Guidelines for Tetramethyllead (See Appendix IV for numbered references.)

Table III-1: Physical-chemical properties for tetramethyllead
(References in Parentheses given in Appendix IV)

TABLE III-1: PHYSICAL-CHEMICAL PROPERTIES		
COMPOUND:	**CHEMICAL FORMULA:**	**CAS No.:**
Tetramethyllead (TML)	$(CH_3)_4Pb$	75-74-1

PROPERTIES	
MOLECULAR WEIGHT (MW):	267.2 g/mol
MELTING POINT:	-27.5°C (2)
BOILING POINT:	108°C (1)
PHYSICAL STATE AT ROOM TEMP.:	liquid
DISSOCIATION CONSTANT (pKa):	non-polar
LIQUID DENSITY (D):	1.995 g/cm^3 @ 25°C (1)
MOLAR VOLUME (MW/D):	135.9 cm^3/mol (2)
VAPOUR PRESSURE (P^s):	3.53 x 10^3 Pa @ 25°C (= 26.5 mmHg) (2)
WATER SOLUBILITY (C^s):	6.7 x 10^{-2} mol/m^3 @ 25°C (= 17.9 mg/L) (3, 2)
HENRY'S LAW (P^s/C^s):	5.27 x 10^4 Pa· m^3/mol (calc.)

OCTANOL-WATER PARTITION COEFFICIENT (K_{ow})	
AVAILABLE Log K_{ow} VALUES:	3.7 (calculated - ref 4)
FINAL CHOSEN Log K_{ow} VALUE:	3.7

BASELINE UNCERTAINTY FACTOR FOR GUIDELINE DEVELOPMENT

IF valid log K_{ow} < 4.0, use 1000

IF valid log K_{ow} ≥ 4.0, use 10 000

BASELINE UNCERTAINTY FACTOR: 1000 ENTERED ON TABLE III-3

Table III-2: AQUATIC TOXIICTY DATA TABLE FOR TETRAMETHYLLEAD

Species	Life Stage	Response Key (1)	Test Solution Parameters					Effect Conc. (ug/L)	Data Codes Key (2)	Ref. No.	Data Quality Key (3)
			pH	Temp. °C	D.O. (mg/L)	Hardness (mg/L CaCO3)	Alkalinity				
VERTEBRATES											
Rainbow trout	fry (1g)	7d LC17	7.86	14.9	8.2	135		3.5	FM	8	SC
Oncorhynchus mykiss	fingerlings (20g)	10d LC20	7.86	14.9	8.2	135		24	FM	8	SA
	fingerlings (20g)	10d LC67	7.86	14.9	8.2	135		51	FM	8	SA
ALGAE											
Scenedesmus quadricaudia		32% growth inhibition 85% decrease in photosynthesis		CHU-10 medium - 500 lux				430*	SU	9	SC
Ankistrodesmus falcatus		32% growth inhibition 49% decrease in photosynthesis		CHU-10 medium - 500 lux				430*	SU	9	SC
Chlorella pyrenoidosa		74% growth inhibition 83% decrease in photosynthesis		CHU-10 medium - 500 lux				430*	SU	9	SC

Key (1)	Key (2)	Key (3)
TLm = Median Tolerance Limit LC = Lethal Concentration IC = Immobilization Concentration EC = Effects Concentration LT50 = Median Lethal Time NOEC = No Observed Effect Concentration * = Calculated from authors data	S = Static F = Flowthrough U = Unmeasured Toxicant Concentration M = Measured Toxicant Concentration R = Renewed Static	P = Primary S = Secondary A = Acute Toxicity C = Chronic Toxicity

Table III-3: UNCERTAINTY FACTOR WORKSHEET

CHEMICAL:	CAS No.	CONCENTRATION UNITS
Tetramethyllead	75-74-1	ug/L

Test Conditions		Species (life stage)	Toxicity End Point	Effect conc.	Data Codes [1]	Data Type [2]	Calibration Factor	No. and Reference
ACUTE	VERTEBRATE	Rainbow trout fingerlings	10d-LC20	24	FM	2°	0.9	Wong et al. 1981 (8)
	INVERT.							
CHRONIC	VERTEBRATE	Rainbow trout, fry	7d-LC17	3.5	FM	2°	0.7	Wong et al. 1981 (8)
	INVERT.							
	PLANT	*Scenedesmus quadricaudia*	32% gr. inhib. 85% p.s. decr.	430	SU	2°	0.9	Silverberg et al. 1977 (9)

CALCULATION OF FINAL UNCERTAINTY FACTOR:

Since Log Kow < 4.00, The Baseline Uncertainty Factor = 1000

Baseline Uncertainty Factor X Calibration Factors (maximum number = 11)

1000 X .9 X .7 X .9 X ___ X ___ X ___ X ___ X ___ X ___ X ___ X ___

= 567 FINAL UNCERTAINTY FACTOR (NOT TO BE LESS THAN A VALUE OF 13)

CRITICAL VALUE ÷ FINAL UNCERTAINTY FACTOR = PWQG OR INTERIM GUIDELINE VALUE

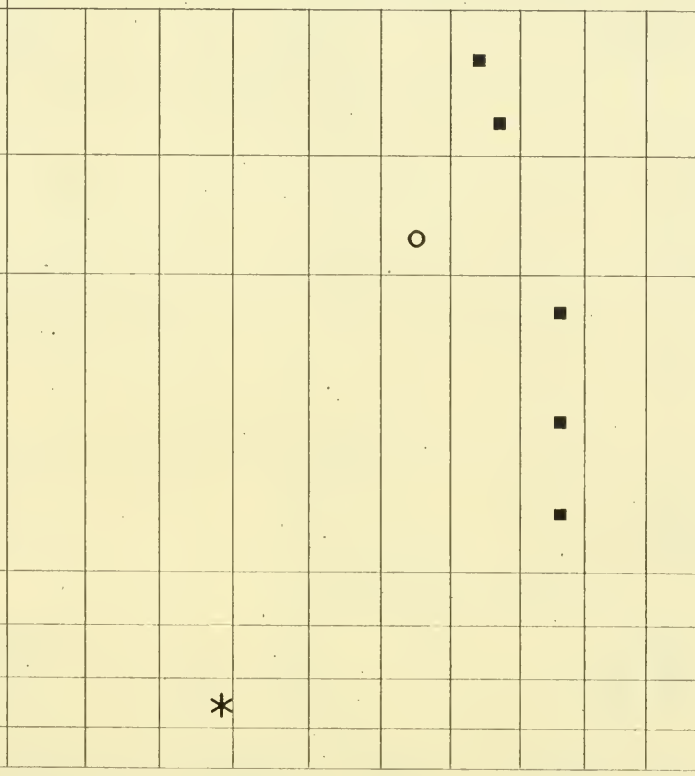
= 3.5 ÷ 567 = 0.006 ug/L

[1] Assign 2 DATA CODES, one from each of the following rows:
C = chronic A = acute
S = static R = static/renewal F = flowthrough
U = unmeasured nominal conc. M = measured conc

[2] DATA TYPE:
1° = Primary 2° = Seconoary 3° = Simulated Data
? = Unknown (Default Data Quality = 2°)

FIG. III-1: GUIDELINE DERIVATION GRAPH - TETRAMETHYLLEAD

Toxicity Information Considered		Species and Life Stage	Exposure and Duration	Ref. No.
ACUTE	Vert.	Rainbow trout fingerlings (20g)	10d LC20	8
		Rainbow trout fingerlings (20g)	10d LC67	8
CHRONIC	Vert.	**Rainbow trout** *Oncorhynchus mykiss* fry (1g)	7d LC17	8
	Plant	*Scenedesmus quadricaudia*	32% growth inhibition, 85% decrease in phytosynthesis	9
		Ankistrodesmus falcatus	32% growth inhibition, 49% decrease in phytosynthesis	9
		Chorella pyrenoidosa	32% growth inhibition, 74% decrease in phytosynthesis	9
taste odour tainting		N.A.		
BCF		N.A.		
PWQG		**Based on critical value of 3.5 ug/L and Final Uncertainty Factor of 567**	0.006ug/L	
Other Agency Objectives			N.A.	



o - Critical Value ■ - Toxicity endpoints ▲ - Objectives of other agencies
✳ -Advisory/PWQG △ - Odour Protection Values

Appendix IV: References for organolead guideline forms

1. Sax and Lewis (1987)
2. Shapiro and Frey (1968)
3. Jensen 1984
4. Chiou *et al.* (1977)
5. Wong *et al.* (1987)
6. Turnbull *et al.* (1954)
7. Roderer (1980)
8. Wong *et al.* (1981)
9. Silverberg *et al.* (1977)
10. Danil'chenko and Stroganov (1975)
11. Roderer (1981)
12. Heumann (1987)
13. Tobias (1978)

Appendix V: Synopsis of Critical Value Papers

Table V-1: Summary details of the "Critical Value" Tests Used in Developing PWQGs for Alkylleads

Chemical	Tetraethyllead	Triethyllead chloride	Tetramethyllead
Reference	Wong et al. 1987	Danil'chenko & Stroganov 1975	Wong et al. 1981
PWQG Data Quality Classification	Secondary	Secondary	Secondary
Common Name	Rainbow trout	Gudgeon and Roach	Rainbow trout
Scientific Name	*Oncorhynchus mykiss*	*Gobio gobio/Rutilus rutilus*	*Oncorhynchus mykiss*
Organism Age/Size	300 gram	Fert. egg through hatching	1 gram
Exposure Duration	Up to 3 weeks	Unspecified. Exposed until 90% dead	7 days
Chronic/Acute	Acute	Chronic	Chronic
Endpoint	Lethality (LT50)	Development / Abnormalities	LC17
Effect Concentration	5 µg/L = 15d-LT50 10 µg/L = 9d-LT50	90 µg/L	3.5 µg/L
Static, renewal or flow-through	Flow-through	Static	Flow-through
Measured/Unmeasured	Measured	Nominal	Measured
# of test concentrations and controls	3 levels + control	7 levels + control	1 level
# of test organisms per concentration	9 fish	150-200 eggs	30 fish
Chemical Purity	Not stated	Not stated	80% TML in toluene
Water type	Filtered L. Ontario	Not stated	Filtered L. Ontario
Temperature (°C)	15°C	Not stated	14.9 ± 0.9°C
pH	Not stated	Not stated	7.86 ± 0.19
Dissolved oxygen (mg/L)	Not stated	Not stated	8.2 ± 1.2
Hardness (mg/L $CaCO_3$)	Not stated	Not stated	135 ± 2.5
Alkalinity (mg/L $CaCO_3$)	Not stated	Not stated	Not stated
Test Container	Not stated	Petri dish	8.1 L test tank
Volume of test solution	Not stated	Not stated	Not stated
Measures taken to prevent volatilization	Not stated	Not stated	Kept in dark bottle and stirred